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Synthesis and Mercuration of Anils of Benzoylferrocene

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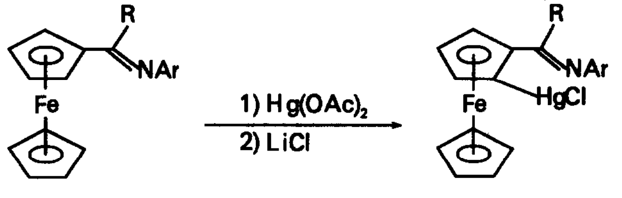
Abstract: *A series of anils of benzoylferrocene were synthesized and characterized to be a mixture of trans and cis isomers in solution, the reaction of which with mercuric acetate gave regioselectively ortho-mercurated products in high yields. On the basis of the NMR data, the related stereochemistry for both the anils and the mercurated compounds has been discussed.*

INTRODUCTION

We have demonstrated that the mercurations of ferrocenylaldimines 1 and ferrocenylketimines 3 occur predominantly on the *ortho*-position of the substituted Cp ring (cyclopentadienyl ring), affording the cyclomercurated ferrocenylimines 2 and 4, respectively[1,2]. Such reactions are of interest in that they will provide a new route, after suitable functional group modification, to inherently chiral 1,2-disubstituted ferrocenes. It has also been found that when R is a methyl group and Ar contains electron-donating group such as OCH_3 or CH_3 in the *para*-position, the yields of the *ortho*-mercurated products are very low, and it appears that the high electron density in the imino nitrogen is quite unfavorable to the mercuration on the *ortho*-position[2]. In the



R = H (1), CH_3(3)   R = H (2), CH_3(4)

light of this work, it was anticipated that the anils of benzoylferrocene, a kind of ferrocenylketimines, would undergo readily mercuration to produce cyclomercurated products in high yield. This paper describes the experiment designed to gain further insight into the substituent effect on the mercuration of ferrocenylimines. Furthermore, the related stereochemistry is also discussed.

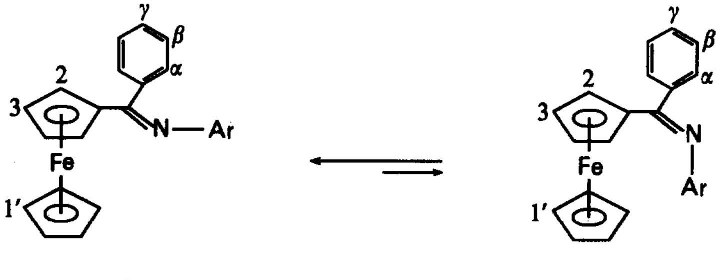
RESULTS AND DISCUSSION

Synthesis and Characterization of **5**

In general, the synthetic pathways to the ferrocenylimines involve the direct reflux of anilines and formylferrocene in ethyl alcohol[3], the synthesis of ferrocenyliminium salts and subsequent deprotonation[4] and the condensation of anilines with acetylferrocene in the presence of activated alumina in anhydrous toluene[5]. The last method is proved to be effective for the synthesis of ferrocenylketimines **5**. All the compounds **5** obtained are first reported ferrocenylimines and were characterized by elemental analyses, IR and ^1H NMR spectra.

The IR spectra of **5** were consistent with a monosubstituted ferrocene structure, showing absorptions at 1000 cm^{-1} and 1100 cm^{-1} which are indicative of an unsubstituted Cp ring[6,7]. The C=N absorptions for **5** appear at *ca.* 1615 cm^{-1}.

The ^1H NMR spectra of **5** indicated that all the compounds exist as two isomers in solution, exhibiting two sets of signals corresponding to the isomers, the ratio of them being about 90:10. It is believed that the isomerism must be attributed to the *trans* and *cis* arrangement of ferrocenyl moiety and the N−aryl ring. The sets of signals in the spectra were completely in accord with the proposed structure, exhibiting expected A_2X_2 system for the protons of the substituted Cp ring, a singlet for five protons of the unsubstituted Cp ring and multiplets for the protons of the C−phenyl ring and the N−aryl ring. The two isomers displayed very different ^1H NMR spectral features, and the differences of chemical shifts for the corresponding protons are listed in Table 1. Compared with the major isomer, the protons for the ferrocenyl moiety of the minor



trans−**5** *cis*−**5**

Ar = *p*−$CH_3OC_6H_4$(a), *p*−$CH_3C_6H_4$(b), C_6H_5(c), *p*−ClC_6H_4(d), *p*−BrC_6H_4(e), *p*−IC_6H_4(f), *m*−$CH_3C_6H_4$(g), *m*−ClC_6H_4(h), *m*−BrC_6H_4(i), *m*−$NO_2C_6H_4$(j), *o*−ClC_6H_4(k), 2−naphthyl(l).

Table 1. $\Delta\delta$ Values for Various Protons of the *trans* and *cis* Isomers ($\Delta\delta = \delta cis - \delta trans$)

Compound	1'	2	3	α	β+γ	Protons for Ar ring	CH_3
5a	−0.22	−0.75	−0.18	0.55	0.17	0.37, 0.37	0.16
5b	−0.11	−0.74	−0.18	0.55	0.19	0.30, 0.22	0.19
5c	−0.11	−0.78	−0.20	0.56	0.20	0.30, 0.24, 0.23	
5d	−0.10	−0.72	−0.17	0.58	0.19	0.31, 0.23	
5e	−0.10	−0.71	−0.16	0.58	0.18	0.29, 0.25	
5f	−0.10	−0.70	−0.16	0.58	0.19	0.30, 0.25	
5g	−0.11	−0.75	−0.18	0.54	0.20	^{a}	0.20
5h	−0.07	−0.72	−0.16	0.56	0.18	0.32, 0.24, 0.32, 0.30	
5i	−0.07	−0.72	−0.16	0.57	0.18	0.16, 0.30 ^{a}	
5j	−0.08	−0.78	−0.19	0.59	0.22	0.24, 0.32 ^{a}	
5k	−0.09	−0.75	−0.18	0.63	0.21	^{a}	
5l	−0.14	−0.81	−0.27	0.57	0.27	0.22, 0.24, 0.25, 0.05, 0.26 ^{a}	

[a]: Some of $\Delta\delta$ values can not be provided due to the spectral overlap.

isomer resonate at higher field, while the protons for both the C−phenyl and N−aryl rings at lower field. The former is attributed to the diamagnetic anisotropic shielding effect of the N−aryl ring in *cis* position to the ferrocenyl moiety, suggesting that the minor isomer corresponds to the *cis* isomer, and the major one thus to the *trans* isomer. The latter can be due to the absence of shielding effect of the N−aryl ring on the protons of the C−phenyl ring and the deshielding effect of ferrocenyl moiety on the N−aryl ring, or probably, the disappearance of the shielding effect of the C−phenyl ring on the N−aryl.

Moreover, in the two isomers, the relative positions of the signals for the protons of the C−phenyl and ferrocenyl moiety are different. In the major isomer, the protons α resonate at higher field in comparison with the protons β and γ, and the protons of the substituted Cp ring at lower field compared with those of the unsubstituted Cp ring. In contrast, in the minor isomer, the protons α resonate at lower field than the protons β and γ, and one of protons 2 and 3 resonates as a triplet at lower field than the protons 1' and the other also as a triplet but at higher field. This can also be explained by taking the ring current effect of the N−aryl ring into account, also consistent with the assignment of the isomers. For minor isomer, the triplet at higher field is assigned to the proton 2, since it should be more shielded by the N−aryl ring.

2D NOESY was measured for **5c** to assign unambiguously the triplets at δ 4.66 and δ 4.42 for the major isomer as well as the triplet at δ 3.90 and δ 4.23 for the minor isomer, and also to find out the dynamic chemical exchange between the isomers. The resulting 2D NMR spectrum illustrates both NOE and chemical exchange between the proton nuclei of the isomers by the distinct symmetrical off−diagonal contour on the NOE map(Figure 1). It was confirmed that the down field triplet at δ 4.66 corresponds to the protons 2 in the *trans* isomer and upfield triplet at δ 3.90 to the protons 2 in the *cis* isomer due to the appearance of negative cross peaks representing the NOE between the protons 2 and the protons of the C−phenyl ring, which was also supported by the exchange of the triplet at δ 4.66 and that at δ 3.90. This result is in

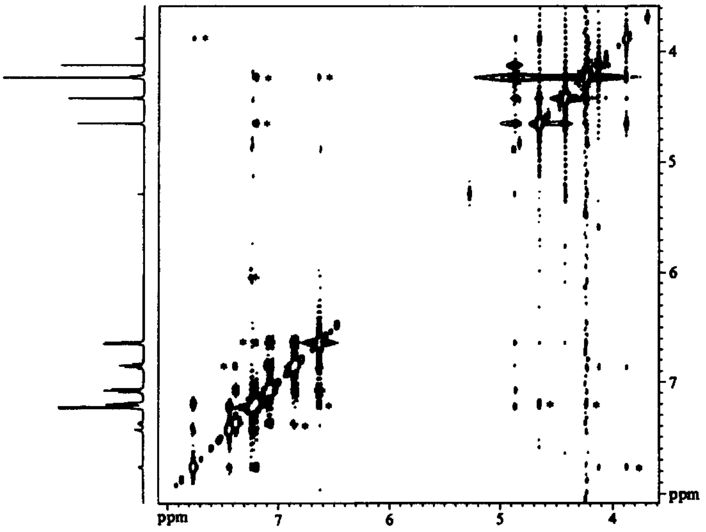
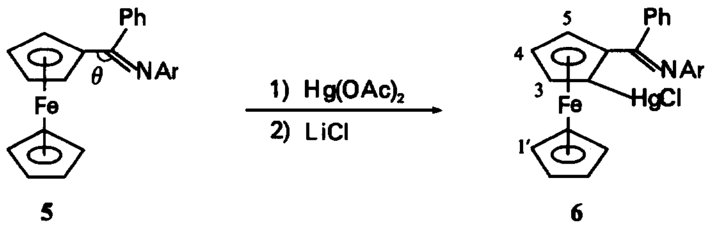


Fig. 1. 2D NOESY spectrum of **5c**. *: NOE peaks.

agreement with the assignment of protons 2 of the minor isomer made above. The cross peaks representing chemical exchange offer a possibility to distinguish the overlapping spectral lines, and thus protons of the N-phenyl in the *cis* isomer was found to resonate at δ 6.87, 7.09 and 7.38 due to the exchange with the corresponding protons for the *trans* isomer. The ^1H NMR spectra of **5** have the similar features, and so the assignment of the other compounds are also similar to that for **5c**.

Mercuration of Ferrocenylketimines **5**

As expected, the acetoxymercuration of **5** followed by the treatment of the resulting products with lithium chloride produced *ortho*-chloromercurated ferrocenylketimines **6** in high yields. In a manner analogous to those of **1** and **3**, the *ortho*-mercuration of **5** should involve the initial coordination of the mercury to the imino nitrogen and subsequent electrophilic substitution, and obviously, only mercuration of the *trans* isomer can be directed by the nitrogen to the *ortho*- position of the substituted Cp ring.



The mercuration results are summerized in Table 2, and it can be noted that the yields and selectivities of **6** show no obvious dependence on the substituents in the N−aryl. But both are much better than those of **2** and **4** reported previously[1,2], indicating the important role played by the C−phenyl. The effect of the phenyl can be due to the fact that the steric repulsion between the C−phenyl and the ferrocenyl moiety as well as the N−aryl leads to smaller angle θ than the normal 120° required for the sp^2 hybridization state and this facilitates the directing of mercury to the *ortho*−position by the nitrogen. In addition, unlike the C−methyl in **3**, the C−phenyl in **5** may weaken the basicity of ferrocenylimines **6**, which is unfavorable to the protonation of the nitrogen by the acetic acid liberated in the reaction but favorable to the coordination of mercury to it[2].

Table 2. Mercuration Results

Compound	**6a**	**6b**	**6c**	**6d**	**6e**	**6f**	**6g**	**6h**	**6i**	**6j**	**6k**	**6l**
yields (%)[a]	81	77	74	66	79	80	74	76	78	76	76	62
Selectivities (%)[b]	96	93	92	90	94	95	85	90	90	92	93	68

[a]: Yields are based on the starting ferrocenylketimines **5**. [b]: Selectivities are based on the consumed **5**.

The IR spectra of the mercurated products **6** showed absorptions at 1100 and 1000 cm^{-1} characteristic of the presence of unsubstituted Cp ring. The C=N absorptions are shifted to lower energy by *ca.* 20 cm^{-1} compared with the unmercurated parent compounds **5**, indicative of intramolecular N → Hg coordination in the molecules[1, 2]. The ^1H NMR spectra of **6** were completely consistent with the proposed structure, exhibiting the expected AMX system for the three different protons on the 1,2−disubstituted Cp ring (a downfield one−proton triplet with J 2.50 and two upfield one−proton doublets of doublets with J 2.55, 1.10 and 2.35, 1.10), and five protons for the unsubstituted Cp ring resonate at higher field. The features of the remainder of the spectra are identical with those for the major isomer of **5**, and this provides further evidence for the assignment of the isomers.

It is noteworthy that the relative positions of the triplet and the doublets of doublets are different from those for the analogous compounds **2** and **4**, indicating that the protons 3 and 5 adjacent to the substituents are more shielded than the proton 4. We have previously found that a chloromercuri group in **2** and **4** tends to shield the proton α to this group to a greater extent than the proton β to it [1, 2], and Roling and Rausch claimed earlier this effect in 1−acetyl−2−chloromercuriferrocene [8], but no ^1H NMR data were found in their related paper [9]. Obviously, the chloromercuri group in **6** also displays the same effect. The other upfield proton must be shielded by the ring current of the C−phenyl, suggesting the more or less perpendicular nature of the substituted Cp ring and the C−phenyl ring. The intramolecular coordination between the imino nitrogen and the mercury would be expected to hold the substituted Cp ring and the plane of −C=N− in coplane, and thus the C−phenyl ring might form a considerable angle with the plane. In order to assign the two upfield doublets of doublets, we decided to record the NOESY spectrum of **6a**, and it was proved that the doublet of doublets at higher field corresponds to the proton 5, because it shows NOE with the protons of the C−phenyl. It can be considered that the shielding effect of the C−phenyl is very large.

EXPERIMENTAL SECTION

General

Melting points were determined using a WC-1 microscopic apparatus and are uncorrected. Elemental analyses were determined on a Calo Erba 1106 Elemental Analysizer. IR spectra were recorded, as KBr pellets, on a Shimadzu 435 Spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker ARX-500 spectrometer in $CDCl_3$. Chemical shifts(δ) are given in ppm relative to that of $CHCl_3$(δ 7.24 ppm), all coupling constants J in hertz. The 2D NOESY spectra were recorded in $CDCl_3$ at room temperature with a mixing time of 400 ms. Chromatographic work was carried out using silica gel packed dry column under reduced pressure.

*Synthesis of Anils of Benzoylferrocene(**5**).*

Molar equivalents of benzoylferrocene and corresponding aniline were refluxed in anhydrous toluene in the presence of activated alumina for about 6 hours and then filtered. The filtration was evaporated to dryness *in vacuo* and the residue crystallized from methylene chloride-petroleum ether(60-90 ℃), affording the ferrocenylketimines **5**.

*[((4-methoxyphenyl)imino)phenylmethyl]ferrocene(***5a***).* Deep red brown crystals, yield 85%; m.p. 176-178 ℃. IR: 1614, 1100, 1000, 826, 700, 772, 1234 cm^{-1}. ^{1}H NMR: δ(*trans*) 4.23 (s, 5H, H-1′), 4.64(t, 2H, J=1.9, H-2), 4.41(t, 2H, J=1.9, H-3), 7.19(m, 2H, H-α), 7.25 (m, 3H, H-β, γ), 6.58(d, 2H, J=8.8, Ar-H), 6.63(d, 2H, J=8.8, Ar-H), 3.68(s, 3H, OCH_3); δ(*cis*) 4.11(s, 5H, H-1′), 3.89(t, 2H, J=2.0, H-2), 4.23(t, 2H, J=2.0, H-3), 7.75(m, 2H, H-α), 7.42 (m, 3H, H-β, γ), 6.80(d, 2H, J=8.8, Ar-H), 6.95(d, 2H, J=9.0, Ar-H), 3.84(s, 3H, OCH_3). Anal. calcd. for $C_{24}H_{21}FeNO$: C, 72.92; H, 5.36; N, 3.54. Found: C, 72.55; H, 5.49; N, 3.65.

*[((4-methylphenyl)imino)phenylmethyl]ferrocene(***5b***).* Orange yellow crystals, yield 75%, m.p. 137-139 ℃. IR: 1616, 1100, 1000, 820, 700, 769 cm^{-1}. ^{1}H NMR: δ(*trans*) 4.23(s, 5H, H-1′), 4.64(t, 2H, J=2.0, H-2), 4.41(t, 2H, J=1.9, H-3), 7.20(m, 2H, H-α), 7.24(m, 3H, H-β, γ), 6.53(d, 2H, J=8.2, Ar-H), 6.87(d, 2H, J=8.0, Ar-H), 2.18(s, 3H, CH_3); δ(*cis*) 4.12 (s, 5H, H-1′), 3.90(t, 2H, J=2.0, H-2), 4.23(t, 2H, J=2.0, H-3), 7.75(m, 2H, H-α), 7.43 (m, 3H, H-β, γ), 6.75(d, 2H, J=8.8, Ar-H), 7.17(d, 2H, J=8.8, Ar-H), 2.37(s, 3H, CH_3) Anal. calcd. for $C_{24}H_{21}FeN$: C, 75.99; H, 5.59; N, 3.69. Found: C, 75.48; H, 5.17; N, 3.95.

*[(phenylimino)phenylmethyl]ferrocene(***5c***).* Red crystals, yield 64%, m.p. 154-155 ℃. IR: 1600, 1103, 998, 818, 696, 768, 772 cm^{-1}. ^{1}H NMR: δ(*trans*) 4.24(s, 5H, H-1′), 4.66(t, 2H, J=1.9, H-2), 4.42(t, 2H, J=1.9, H-3), 7.20(m, 2H, H-α), 7.23(m, 3H. H-β, γ), 6.64(d, 2H, J=8.3, Ar-H), 6.85(t, 1H, J=7.4, Ar-H), 7.08(t, 2H, J=8.2, Ar-H); δ(*cis*) 4.13(s, 5H, H-1′), 3.88(t, 2H, J=2.0, H-2), 4.22(t, 2H, J=2.0, H-3), 7.76(m, 2H, H-α), 7.43(m, 3H, H-β, γ), 6.87 (d, 2H, J=7.8, Ar-H), 7.09(1H, Ar-H), 7.38(t, 2H, J=8.6, Ar-H). Anal. calcd. for $C_{23}H_{19}FeN$: C, 75.62; H, 5.25; N, 3.84. Found: C, 75.26; H, 5.18; N, 3.74.

*[((4-chlorophenyl) imino) phenylmethyl]ferrocene (***5d***).* Brown crystals, yield 62%, m. p. 147-149 ℃. IR: 1616, 1100, 1000, 824, 696, 760cm^{-1}. ^{1}H NMR: δ(*trans*) 4.23 (s, 5H, H-1′), 4.64 (t, 2H, J=2.0, H-2), 4.44(t, 2H, J=1.9, H-3), 7.17(m, 2H, H-α), 7.25(m, 3H, H-β, γ), 6.57 (d, 2H, J=8.6, Ar-H), 7.03 (d, 2H, J=8.6, Ar-H); δ (*cis*) 4.13 (s, 5H, H-1′), 3.92 (t, 2H, J=2.0,

H-2), 4.27(t, 2H, J=2.0, H-3), 7.75(m, 2H, H-α), 7.44(m, 3H, H-β, γ), 6.80(d, 2H, J=8.6, Ar-H), 7.34(d, 2H, J=8.6, Ar-H). Anal. calcd. for $C_{23}H_{18}ClFeN$: C, 69.11; H, 4.55; N, 3.50. Found: C, 68.76; H, 4.56; N, 4.00.

[((4-bromophenyl)imino)phenylmethyl]ferrocene (5e). Brown crystals, yield 67%, m. p. 158-159 ℃. IR: 1616, 1100, 1002, 823, 696, 760cm^{-1}. ^{1}H NMR: δ(*trans*) 4.23(s, 5H, H-1'), 4.64 (t, 2H, J=2.0, H-2), 4.44(t, 2H, J=1.9, H-3), 7.17(m, 2H, H-α), 7.25(m, 3H, H-β, γ), 6.51 (d, 2H, J=8.6, Ar-H), 7.19 (d, 2H, J=8.6, Ar-H); δ(*cis*) 4.13 (s, 5H, H-1'), 3.93 (t, 2H, J=2.0, H-2), 4.28(t, 2H, J=2.0, H-3), 7.75(m, 2H, H-α), 7.43(m, 3H, H-β, γ), 6.76(d, 2H, J=8.6, Ar-H), 7.48(d, 2H, J=8.6, Ar-H). Anal. calcd. for $C_{23}H_{18}BrFeN$: C, 62.19; H, 4.09; N, 3.15. Found: C, 62.06; H, 4.11; N, 3.20.

[((4-iodophenyl)imino)phenylmethyl]ferrocene(5f). Brown crystals, yield 65%, m.p. 159-160 ℃. IR: 1614, 1100, 1000, 820, 696, 760 cm^{-1}. ^{1}H NMR: δ(*trans*) 4.23(s, 5H, H-1'), 4.63(t, 2H, J=1.9, H-2), 4.44(t, 2H, J=1.9, H-3), 7.17(m, 2H, H-α), 7.26(m, 3H, H-β, γ), 6.40 (d, 2H, J=8.5, Ar-H), 7.36(d, 2H, J=8.5, Ar-H); δ(*cis*) 4.13(s, 5H, H-1'), 3.93(t, 2H, J=1.9, H-2), 4.28(t, 2H, J=2.0, H-3), 7.75(m, 2H, H-α), 7.44(m, 3H, H-β, γ), 6.65(d, 2H, J=8.4, Ar-H), 7.66(d, 2H, J=8.4, Ar-H). Anal. calcd. for $C_{23}H_{18}FeIN$: C, 56.24; H, 3.70; N, 2.85. Found: C, 55.91; H, 3.42; N, 2.82.

[((3-methylphenyl)imino)phenylmethyl]ferrocene (5g). Brown crystals, yield 60%, m. p. 100-102 ℃. IR: 1616, 1102, 1000, 820, 698, 766, 782 cm^{-1}. ^{1}H NMR: δ(*trans*) 4.24(s, 5H, H-1'), 4.65(t, 2H, J=2.0, H-2), 4.41(t, 2H, J=1.9, H-3), 7.19-7.24(m, 5H, H-α, β, γ), 6.38 (d, 1H, J=7.9, Ar-H), 6.51 (s, 1H, Ar-H), 6.66 (d, 1H, J=7.6, Ar-H), 6.94 (t, 1H, J=7.7, Ar-H), 2.18(s, 3H, CH_3); δ(*cis*) 4.13(s, 5H, H-1'), 3.90(t, 2H, J=2.0, H-2), 4.23(t, 2H, J=2.0, H-3), 7.75(m, 2H, H-α), 7.44(m, 3H, H-β, γ), 2.38(s, 3H, CH_3). Anal. calcd. for $C_{24}H_{21}FeN$: C, 75.99; H, 5.59; N, 3.69. Found: C, 75.73; H, 5.51; N, 3.92.

[((3-chlorophenyl)imino)phenylmethyl]ferrocene(5h). Red crystals, yield 56%, m.p. 132-133 ℃. IR: 1614, 1104, 1000, 820, 700, 766, 787 cm^{-1}. ^{1}H NMR: δ(*trans*) 4.23(s, 5H, H-1'), 4.64 (t, 2H, J=2.0, H-2), 4.44(t, 2H, J=2.0, H-3), 7.19(m, 2H, H-α), 7.26(m, 3H, H-β, γ), 6.46 (d, 1H, J=7.9, Ar-H), 6.69(t, 1H, J=2.0, Ar-H), 6.83(d, 1H, J=8.0, Ar-H), 6.98(t, 1H, J=8.5, Ar-H); δ(*cis*) 4.16(s, 5H, H-1'), 3.92(t, 2H, J=2.0, H-2), 4.28(t, 2H, J=2.0, H-3), 7.75 (m, 2H, H-α), 7.44 (m, 3H, H-β, γ), 6.76 (d, 1H, J=8.6, Ar-H), 6.91 (s, 1H, Ar-H), 7.07 (d, 1H, J=8.6, Ar-H), 7.30(t, 1H, J=8.6, Ar-H). Anal. calcd. for $C_{23}H_{18}ClFeN$: C, 69.11; H, 4.55; N, 3.50. Found: C, 68.89; H, 4.38; N, 3.23.

[((3-bromophenyl)imino)phenylmethyl]ferrocene (5i). Brown crystals, yield 60%, m. p. 121-122 ℃. IR: 1614, 1104, 1000, 820, 706, 764, 784 cm^{-1}. ^{1}H NMR: δ(*trans*) 4.23(s, 5H, H-1'), 4.64(t, 2H, J=2.0, H-2), 4.44(t, 2H, J=2.0, H-3), 7.19(m, 2H, H-α), 7.27(m, 3H, H-β, γ), 6.50(d, 1H, J=8.6, Ar-H), 6.85(t, 1H, J=2.0, Ar-H), 6.91(t, 1H, J=7.7, Ar-H), 6.98(d, 1H, J=8.5, Ar-H); δ(*cis*) 4.16(s, 5H, H-1'), 3.92(t, 2H, J=2.0, H-2), 4.28(t, 2H, J=2.0, H-3), 7.75(m, 2H, H-α), 7.44(m, 3H, H-β, γ), 6.80(d, 1H, J=8.6, Ar-H), 7.07(s, 1H, Ar-H). Anal. calcd. for $C_{23}H_{18}BrFeN$: C, 62.19; H, 4.09; N, 3.15. Found: C, 62.01; H, 4.03; N, 3.39.

[((3-nitrophenyl)imino)phenylmethyl]ferrocene(5j). Red crystals, yield 50%, m.p. 156-157 ℃. IR: 1604, 1102, 1000, 826, 710, 764, 800, 1520, 1356 cm^{-1}. ^{1}H NMR: δ(*trans*) 4.25(s, 5H, H-1'), 4.66(t, 2H, J=1.9, H-2), 4.49(t, 2H, J=1.9, H-3), 7.17(m, 2H, H-α), 7.24(m, 3H, H-

β, γ), 6.91(d, 1H, J=8.1, Ar−H), 7.21(t, 1H, J=8.1, Ar−H), 7.51(t, 1H, J=2.1, Ar−H), 7.72(d, 1H, J=8.2, Ar−H); δ(*cis*) 4.17(s, 5H, H−1′), 3.88(t, 2H, J=2.0, H−2), 4.30(t, 2H, J=1.9, H−3), 7.76(m, 2H, H−α), 7.46(m, 3H, H−β, γ), 7.53(t, 1H, J=8.6, Ar−H), 7.96(d, 1H, J=8.5, Ar−H). Anal. calcd. for $C_{23}H_{18}FeN_2O_2$: C, 67.33; H, 4.43; N, 6.83. Found: C, 67.44; H, 4.36; N, 7.09.

[((2−chlorophenyl) imino) phenylmethyl]ferrocene (5k). Brown crystals, yield 56%, m. p. 128−129 ℃ . IR: 1608, 1103, 1000, 820, 698, 772, 730 cm^{-1}. ^{1}H NMR: δ(*trans*) 4.27(s, 5H, H−1′) , 4.70 (t, 2H, J=1.9, H−2), 4.45 (t, 2H, J=1.9, H−3), 7.24 (m, 5H, H−α, β, γ), 6.37 (d, 1H, J=7.8, Ar−H), 6.79(d, 1H, J=8.4, Ar−H), 6.88(t, 1H, J=7.6, Ar−H), 7.26(d, 1H, J=8.0, Ar−H); δ(*cis*) 4.18(s, 5H, H−1′), 3.95(t, 2H, J=2.0, H−2), 4.27(t, 2H, J=2.0, H−3), 7.85(m, 2H, H−α), 7.46(m, 3H, H−β, γ). Anal. calcd. for $C_{23}H_{18}ClFeN$: C, 69.11; H, 4.55; N, 3.50. Found: C, 68.82; H, 4.66; N, 3.70.

[((2−naphthyl)imino)phenylmethyl]ferrocene(5l). Brown crystals, yield 66%, m.p. 174−175 ℃. IR: 1610, 1100, 1000, 815, 700, 748 cm^{-1}. ^{1}H NMR: δ(*trans*) 4.27(s, 5H, H−1′), 4.70(t, 2H, J=1.7, H−2), 4.45 (t, 2H, J=1.9, H−3), 7.24 (m, 2H, H−α), 7.19 (m, 3H, H−β, γ), 6.84 (d, 1H, J=8.6, Ar−H), 7.06(d, 1H, J=1.4, Ar−H), 7.28(t, 1H, J=7.0, Ar−H), 7.34(t, 1H, J=7.0, Ar−H), 7.54(d, 1H, J=8.6, Ar−H), 7.60(d, 1H, J=8.1, Ar−H), 7.66(d, 1H, J=7.6, Ar−H); δ(*cis*) 4.13(s, 5H, H−1′), 3.89(t, 2H, J=2.0, H−2), 4.18(t, 2H, J=2.0, H−3), 7.81 (m, 2H, H−α), 7.46(m, 3H, H−β, γ), 7.10(d, 1H, J=8.6, Ar−H), 7.39(t, 1H, J=7.8, Ar−H), 7.79(d, 1H, J=8.6, Ar−H), 7.84(d, 1H, J=8.6, Ar−H), 7.88(d, 1H, J=8.6, Ar−H). Anal. calcd. for $C_{27}H_{21}FeN$: C, 78.08; H, 5.11; N, 3.37. Found: C, 78.06; H, 4.84; N, 3.49.

Mercuration of Ferrocenylketimines 5

The details of the equimolar mercuration reaction, the separation of reaction mixture and the purification procedures are similar to those described previously[1].

2−chloromercurio−1−[((4−methoxyphenyl)imino)phenylmethyl]ferrocene(6a). Red crystals, m.p. 214−216 ℃ (dec) . IR: 1604, 1100, 1000, 820, 698, 770, 1240 cm^{-1}. ^{1}H NMR: δ 4.23 (s, 5H, H−1′), 4.38(dd, 1H, J=2.6, 1.2, H−5), 4.49(dd, 1H, J=2.4, 1.1, H−3), 4.56(t, 1H, J=2.5, H−4), 7.21(m, 2H, H−α), 7.33(m, 3H, H−β, γ), 6.65(m, 4H, Ar−H), 3.70(s, 3H, CH_3), Anal. calcd. for $C_{24}H_{20}ClFeHgNO$: C, 45.73; H, 3.20; N, 2.22. Found: C, 45.81; H, 3.21; N, 2.27.

2−chloromercurio−1− [((4−methylphenyl)imino)phenylmethyl]ferrocene(6b). Red crystals, m.p. 213−214 ℃ (dec) . IR: 1590, 1102, 998, 814, 698, 770 cm^{-1}. ^{1}H NMR: δ 4.23 (s, 5H, H −1′), 4.40(dd, 1H, J=2.6, 1.1, H−5), 4.50(dd, 1H, J=2.3, 1.1, H−3), 4.57(t, 1H, J=2.5, H−4), 7.21(m, 2H, H−α), 7.32(m, 3H, H−β, γ), 6.58(d, 2H, J=8.0, Ar−H), 6.90(d, 2H, J=8.0, Ar−H), 2.20(s, 3H, CH_3). Anal. calcd. for $C_{24}H_{20}ClFeHgN$: C, 46.93; H, 3.29; N, 2.28. Found: C, 46.43; H, 3.02; N, 2.14.

2−chloromercurio−1−[(phenylimino)phenylmethyl]ferrocene(6c). Red crystals, m.p. 216−218 ℃ (dec). IR: 1590, 1102, 1000, 815, 696, 770 cm^{-1}. ^{1}H NMR: δ 4.24(s, 5H, H−1′), 4.42(dd, 1H, J=2.6, 1.2, H−5), 4.52(dd, 1H, J=2.3, 1.0, H−3), 4.59(t, 1H, J=2.5, H−4), 7.20(m, 2H, H−α), 7.30(m, 3H, H−β, γ), 6.67(d, 2H, J=7.4, Ar−H), 6.92(t, 1H, J=7.4, Ar−H), 7.11(t, 2H, J=7.9, Ar−H). Anal. calcd. for $C_{23}H_{18}ClFeHgN$: C, 46.02; H, 3.03; N, 2.33. Found: C, 45.80; H, 2.88; N, 2.17.

*2−chloromercurio−1−[((4−chlorophenyl)imino)phenylmethyl]ferrocene(***6d***).* Red crystals, m.p. 212−213 ℃ (dec). IR: 1590, 1102, 1000, 820, 700, 770 cm^{-1}. ^{1}H NMR: δ 4.23(s, 5H, H−1′), 4.42 (dd, 1H, J=2.6, 1.0, H−5), 4.53 (dd, 1H, J=2.4, 1.0, H−3), 4.60 (t, 1H, J=2.5, H−4), 7.18 (m, 2H, H−α), 7.33 (m, 3H, H−β, γ), 6.60 (d, 2H, J=8.7, Ar−H), 7.06 (d, 2H, J=8.7, Ar−H). Anal. calcd. for $C_{23}H_{17}Cl_2FeHgN$: C, 43.52; H, 2.70; N, 2.21. Found: C, 43.61; H, 2.74; N, 2.57.

*2−chloromercurio−1−[((4−bromophenyl)imino)phenylmethyl]ferrocene(***6e***).* Red crystals, m.p. 217−219 ℃ (dec). IR: 1590, 1102, 1000, 817, 698, 768 cm^{-1}. ^{1}H NMR: δ 4.23(s, 5H, H−1′), 4.42 (dd, 1H, J=2.6, 1.1, H−5), 4.53 (dd, 1H, J=2.4, 1.1, H−3), 4.61 (t, 1H, J=2.4, H−4), 7.18 (m, 2H, H−α), 7.33 (m, 3H, H−β, γ), 6.55 (d, 2H, J=8.7, Ar−H), 7.21 (d, 2H, J=8.7, Ar−H). Anal. calcd. for $C_{23}H_{17}BrClFeHgN$: C, 40.68; H, 2.53; N, 2.06. Found: C, 40.26; H, 2.35; N, 2.30.

*2−chloromercurio−1−[((4−iodophenyl)imino)phenylmethyl]ferrocene(***6f***).* Deep red crystals, m.p. 214−216 ℃ (dec). IR: 1590, 1102, 1000, 817, 698, 764 cm^{-1}. ^{1}H NMR: δ 4.23 (s, 5H, H−1′), 4.42(dd, 1H, J=2.6, 1.0, H−5), 4.53(dd, 1H, J=2.4, 1.0, H−3), 4.61 (t, 1H, J=2.4, H−4), 7.18(m, 2H, H−α), 7.33(m, 3H, H−β, γ), 6.43(d, 2H, J=8.6, Ar−H), 7.40(d, 2H, J=8.6, Ar−H). Anal. calcd. for $C_{23}H_{17}ClFeHgIN$: C, 38.04; H, 2.36; N, 1.93. Found: C, 37.72; H, 2.24; N, 2.02.

*2−chloromercurio−1−[((3−methylphenyl) imino) phenylmethyl]ferrocene (***6g***).* Red crystals, m.p. 194−196 ℃. IR: 1590, 1102, 998, 818, 704, 768, 781 cm^{-1}. ^{1}H NMR: δ 4.23(s, 5H, H−1′), 4.41(dd, 1H, J=2.6, 1.0, H−5), 4.51(dd, 1H, J=2.4, 1.0, H−3), 4.58(t, 1H, J=2.4, H−4), 7.20(m, 2H, H−α), 7.30(m, 3H, H−β, γ), 6.42(d, 1H, J=7.3, Ar−H), 6.55(s, 1H, Ar−H), 6.73 (d, 1H, J=7.5, Ar−H), 6.96 (t, 1H, J=7.8, Ar−H), 2.18 (s, 3H, CH_3). Anal. calcd. for $C_{24}H_{20}ClFeHgN$: C, 46.93; H, 3.29; N, 2.28. Found: C, 46.88; H, 2.85; N, 2.52.

*2−chloromercurio−1−[((3−chlorophenyl)imino)phenylmethyl]ferrocene(***6h***).* Red crystals, m.p. 209−211 ℃ (dec). IR: 1580, 1102, 1000, 814, 710, 774 cm^{-1}. ^{1}H NMR: δ 4.24(s, 5H, H−1′), 4.43(dd, 1H, J=2.6, 1.1, H−5), 4.54(dd, 1H, J=2.4, 1.0, H−3), 4.61(t, 1H, J=2.4, H−4), 7.19(m, 2H, H−α), 7.33(m, 3H, H−β, γ), 6.54(d, 1H, J=8.0, Ar−H), 6.66(t, 1H, J=2.0, Ar−H), 6.89(d, 1H, J=8.0, Ar−H), 7.02(t, 1H, J=8.0, Ar−H). Anal. calcd. for $C_{23}H_{17}Cl_2FeHgN$: C, 43.52; H, 2.70; N, 2.21. Found: C, 43.50; H, 2.49; N, 2.41.

*2−chloromercurio−1−[((3−bromophenyl)imino)phenylmethyl]ferrocene(***6i***).* Red Crystals, m.p. 207−208 ℃ (dec). IR: 1580, 1102, 1000, 812, 708, 770 cm^{-1}. ^{1}H NMR: δ 4.24(s, 5H, H−1′), 4.43(dd, 1H, J=2.6, 1.1, H−5), 4.54(dd, 1H, J=2.4, 1.1, H−3), 4.61(t, 1H, J=2.5, H−4), 7.18(m, 2H, H−α), 7.33(m, 3H, H−β, γ), 6.59(d, 1H, J=8.0, Ar−H), 6.81(t, 1H, J=1.9, Ar−H), 6.97 (t, 1H, J=8.0, Ar−H), 7.05 (d, 1H, J=8.0, Ar−H). Anal. calcd. for $C_{23}H_{17}BrClFeHgN$: C, 40.68; H, 2.53; N, 2.06. Found: C, 40.71; H, 2.40; N, 2.09.

*2−chloromercurio−1−[((3−nitrophenyl)imino)phenylmethyl]ferrocene(***6j***).* Deep red crystals, m.p. 223−225 ℃(dec). IR: 1584, 1102, 1000, 804, 708, 740, 1518, 1348 cm^{-1}. ^{1}H NMR: δ 4.27 (s, 5H, H−1′), 4.46(dd, 1H, J=2.6, 1.1, H−5), 4.58(dd, 1H, J=2.4, 1.0, H−3), 4.66(t, 1H, J=2.5, H−4), 7.18(m, 2H, H−α), 7.33(m, 3H, H−β, γ), 7.03(d, 1H, J=8.2, Ar−H), 7.28 (t, 1H, J=8.2, Ar−H), 7.44 (t, 1H, J=2.2, Ar−H), 7.78 (d, 1H, J=8.2, Ar−H). Anal. calcd. for $C_{23}H_{17}ClFeHgN_2O_2$: C, 42.81; H, 2.66; N, 4.34. Found: C, 42.71; H, 2.51; N, 4.47.

*2−chloromercurio−1−[(2−chlorophenyl) imino) phenylmethyl]ferrocene (***6k***).* Orange crystals, m.p. 214−215 ℃ (dec). IR: 1595, 1102, 1002, 815, 699, 760 cm^{-1}. ^{1}H NMR: δ 4.27(s, 5H, H−1′), 4.47(dd, 1H, J=2.6, 1.0, H−5), 4.55(dd, 1H, J=2.3, 1.0, H−3), 4.62(t, 1H, J=2.5, H−4), 7.18(m, 2H, H−α), 7.28(m, 3H, H−β, γ), 6.23(m, 1H, Ar−H), 6.85(m, 2H, Ar−H), 7.32 (m, 1H, Ar−H), Anal. calcd. for $C_{23}H_{17}Cl_2FeHgN$: C, 43.52; H, 2.70; N, 2.21. Found: C, 43.29; H, 2.55; N, 2.23.

*2−chloromercurio−1−[(2−naphthyl)imino)phenylmethyl]ferrocene(***6l***).* Deep red crystals, m.p. 210−212 ℃ (dec). IR: 1586, 1102, 1000, 820, 700, 746 cm^{-1}. ^1H NMR: δ 4.27(s, 5H, H−1′), 4.46(dd, 1H, J=2.6, 1.0, H−5), 4.54(dd, 1H, J=2.4, 1.1, H−3), 4.62(t, 1H, J=2.5, H−4), 7.28 (m, 2H, H−α), 7.24(m, 3H, H−β, γ), 6.82(d, 1H, J=8.6, Ar−H), 7.16(d, 1H, J=1.9, Ar−H), 7.31(t, 1H, J=7.6, Ar−H), 7.36(t, 1H, J=7.6, Ar−H), 7.55(d, 1H, J=8.8, Ar−H), 7.64(d, 1H, J=7.6, Ar−H), 7.69(d, 1H, J=7.6, Ar−H). Anal. calcd. for $C_{27}H_{20}ClFeHgN$: C, 49.87; H, 3.11; N, 2.15. Found: C, 49.51; H, 2.77; N, 2.33.

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REFERENCES

1. Huo, S.Q.; Wu, Y.J.; Zhu, Y.; Yang, L., *J. Organomet. Chem.*, **1994**, 470, 17.
2. Wu, Y.J.; Huo, S.Q.; Zhu, Y.; Yang, L., *J. Organomet. Chem.*, accepted.
3. Kozlov, N.S.; Kalennikov, E.A.; Kocherevskaya, F.B., *Zh. Org. Khim.*, **1974**, 10, 1024.
4. Cully, N.; Watts, W.E., *Synth. React. Inorg. Met.−Org. Chem.*, **1980**, 10, 289.
5. Ma, H. R.; Yang, B. Q.; Gao, S. L.; Li, D. X.; Zhang, H. L.; Zhang, X. L., *Xibei Daxue Xuebao, Ziran Kexueban*, **1990**, 20, 45.
6. Rosenblum, M.; Woodward, R.B., *J. Am. Chem. Soc.*, **1958**, 80, 5443.
7. Rinehart, K.L.; Motz, Jr.K.L.; Moon, S., *J. Am. Chem. Soc.*, **1957**, 79, 2749.
8. Roling, P.; Rausch, M.D., *J. Org. Chem.*, **1974**, 39, 1420.
9. Kovar, R.F.; Rausch, M.D., *J. Organomet. Chem.*, **1972**, 35, 351.

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